Semiannual Research Summary (3/1/70)

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RADIOLYTIC GRAFTING OF MONOMERS ON POLYMETHYLPENTENE FILM

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I. Introduction

Polymethylpentene film was the initial choice of polymer substrate to be used in this investigation for two reasons. First, little or no work on the grafting of monomers to PMP film has been published. Second, comparison of the grafting behavior of poly(4-methylpentene-1) with other hydrocarbon polymers such as polyethylene and polypropylene should lead to useful conclusions.

The unit structures of the chains of polymethylpentene, polyethylene, and polypropylene are shown in Figure 1. Opposite each branch is a tertiary hydrogen atom. Tertiary hydrogen has been associated by many investigators with the easy formation of polymeric radicals. The unit structure of polypropylene bears one tertiary hydrogen atom for every three carbon atoms, and the same ratio exists in polymethylpentene. The unusual feature in polymethylpentene is that only 50 percent of the tertiary hydrogens are located on the main chain, while the other 50 percent are located on side chains. Although not shown by the polyethylene unit structure, it is well known that polyethylene contains minor amounts of chain branching as revealed by infrared studies and other evidence. If the presence of tertiary hydrogen is related to ease of radical formation and grafting, the differences in branching of the three polymers should lead to differences in grafting behavior.

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The work done to date consists mainly in the construction of apparatus and in the survey of various monomers to determine which ones will graft on PMP film.

II. Experimental Procedure

The 0.5 curie cobalt 60 source was designed in the form of a hollow cylinder, very similar to the one described by Daniels (1). The purpose of the design is to provide usefully high radiation intensity in the center of the cylinder, while keeping the total source strength low enough to avoid the need for extensive shielding facilities. Ferrous sulfate dosimetry (2) was used to determine the radiation dose rate in the center of the cylinder at the location where the film grafting reactions were run. The average of two determinations gave a dose rate of 842 r/hr at that point.

Before use, each monomer was distilled and stored over Drierite at refrigerator temperature. Just prior to making a grafting run, the monomer was outgassed by means of the high vacuum system shown in Figure 2. The procedure involved several successive cycles of freezing the monomer, pumping down, and thawing the monomer again. In the last step, the monomer was transferred to the film capsule surrounded by a dry ice bath. The capsule was then hermetically sealed off at point A with a hand torch. The capsule containing film and monomer was then placed inside the cobalt 60 cylinder, reproducibility of location being assured by the use of a special guide tube and spacer.

Each film sample was approximately 0.5 cm by 2.0 cm in area. After completion of the grafting run, each polymer film was extracted by stirring in warm benzene for 48 hours, then dried in air and weighed. The purpose of this technique was to remove homopolymer formed in or on the film. The procedure used has been found reasonably successful in this regard by several investigators (3,4,5). A correction for film weight loss during extraction was made by running a blank (ungrafted) film through the extraction and drying procedure. All grafting runs were carried out at the temperature of the irradiation room ($23 \pm 1^{\circ}C$).

Percent grafting was computed from corrected film weight (P_o) prior to grafting, and weight after grafting (P_g) as follows:

$$\text{Percent Grafting} = \left[\frac{P_g - P_o}{P_o}\right] \times 100 \qquad (1)$$

In several cases the weight of the swollen film (P_s) at the end of the run was determined by quickly drying the film between filter papers and weighing it in a weighing bottle. This procedure led to some variability in results, since there was a slight variation in the amount of liquid monomer removed from the swollen film by the filter paper. Percent swelling uncorrected for grafting was calculated as follows:

$$\text{Percent Swelling} = \left[\frac{P_s - P_o}{P_o}\right] \times 100 \qquad (2)$$

A special apparatus for grafting monomer vapor to film was also constructed (Figure 3). In making a vapor phase run, the apparatus will be connected to the vacuum line at point A. After outgassing the monomer in the usual way, the desired pressure of oxygen-free monomer vapor will be introduced into the apparatus shown in Figure 3. The whole apparatus will be cut from the vacuum line at A, taken to the irradiation room, and the film capsule inserted into the horizontal cylindrical cobalt source. As the film takes up monomer vapor, the decrease in vapor pressure will be followed telescopically on the manometer. Construction of this special apparatus is now complete, but vapor phase grafting runs have not yet been made.

III. Results and Discussion.

Results obtained to date include a comparison of the grafting behavior of PMP and polyethylene, a comparison of monomer grafting on PMP film, the correlation of percent swelling with percent grafting, and a study of the effect of changing the film thickness of PMP.

A. Comparison of Polymers.

The grafting of styrene monomer on polymethylpentene and polyethylene is compared in Figure 4. The percent grafting versus time curve is linear for both polymethylpentene and polyethylene, at least in the initial portion of the curve. The higher percentage of branching (tertiary hydrogen) in PMP does not produce a higher rate of grafting than for polyethylene. This indicates that the presence of tertiary hydrogen is not the predominant factor in determining ease of grafting. However, such evidence does not rule out the possibility that the presence of tertiary hydrogen may be one of the factors which influences grafting. (A comparison curve showing grafting of styrene on polypropylene is in the process of preparation.)

It is recognized that a comparison of rates at a single temperature is not as significant as a comparison of activation energies based on rate measurements at a series of temperatures. Temperature control equipment is now being obtained, which will enable the measurement of energies of activation.

B. Comparison of Monomers.

Rates of grafting of styrene, methyl methacrylate, and acrylonitrile on PMP film were studied. Grafting of styrene and methyl methacrylate is shown in Figure 5, but the amount of acrylonitrile grafted was too small to measure under the conditions employed. Polymethylpentene film swelled visibly in styrene and

methyl methacrylate, but showed no apparent swelling in acrylonitrile. The absence of swelling in acrylonitrile may be related to the absence of grafting in that monomer.

While PMP film does not swell appreciably in liquid acrylonitrile, it has been found to swell in solutions of acrylonitrile in benzene. Runs will be carried out in such solutions to determine if grafting on PMP film takes place under such conditions.

The autocatalytic character of the methyl methacrylate curve (Figure 5) has also been observed in the grafting of methyl methacrylate on polyethylene (6).

C. Relation of Grafting to Swelling.

Figure 6 plots percent grafting against percent swelling for 0.0055 inch polymethylpentene and 0.009 inch polyethylene in styrene. The figure shows that the relationship is linear in these cases. Similar calculations were made for 0.0107 inch PMP in styrene, but a clearcut linear relationship was not obtained. Previous investigators have presented a variety of opinions on the relationship of grafting to swelling, but most appear to regard swelling as one of the factors involved in grafting (7).

It was noted above that PMP film does not swell appreciably in liquid acrylonitrile, and also shows no grafting by acrylonitrile under the conditions employed. The absence of grafting may be related to the lack of swelling.

D. Diffusion Effect on Grafting Rate.

Several investigators have remarked that monomer may graft only in the surface layer of thicker films, and fail to penetrate to the center of the film. Such a diffusion limitation would lower the apparent amount of monomer grafting on the thicker films, expressed as a percentage of total film weight.

A test of this effect for the grafting of styrene on PMP film is presented in Figure 7, which compares the behavior of 0.0055 and 0.0107 inch film. The grafting rate shows a slight decrease for the thicker film, but the decrease is probably within experimental error. Certainly the diffusion limitation is not a major factor under these experimental conditions.

IV. Theoretical Background.

A. General Discussion.

While Figure 7 does not show much of a decrease in rate for thicker film due to the slowness of monomer diffusion, it is quite likely that the effect will show up in some phase of the present investigation. Most writers in this field have mentioned the effect of the diffusion limitation, and some have discussed it extensively.

For example, Hoffman (3) carried out radiolytic grafting of styrene on polyethylene film, and postulated that monomer concentration within the film may decrease during grafting due to the inability of the diffusion of monomer into the film to keep pace with its rate of reaction in the film. In line with this postulate, he observed that grafting was faster for thin films than for thick films on the basis of percentage of total film weight. He introduced the idea of a critical film thickness, above which the rate of grafting on a weight percentage basis should fall off rapidly.

Chapiro (7) found that the rate of grafting of styrene on polyvinylchloride film at 20°C was entirely controlled by the rate of diffusion of monomer into the interior of the film. When the reaction temperature was increased to 60°C, the monomer diffused into the film more rapidly, reaction rate was no longer limited by diffusion rate, and the reaction kinetics became "normal".

The situation that probably exists inside the polymer film can be illustrated by reference to Figure 8, which compares a thin film (A) with a much thicker film (B). Considering film (A) first, the solid curve shows the monomer concentration plotted versus film thickness after a constant rate of grafting is attained (linear portion of grafting versus time curve). The concentration of monomer has not quite reached zero at the center of the film, but it is much lower than at the film surface. The dotted line indicates the equilibrium concentration, C_o , which would be the uniform concentration attained if the film were simply immersed in monomer and allowed to become saturated with monomer in the absence of the grafting reaction.

In the thicker film (B) the monomer reacts and is consumed before it can diffuse to the center of the film. The supply of monomer in a considerable portion of the center of the film is completely exhausted. Under these circumstances, the monomer penetrates to a limited depth, d, and all of the grafting takes place within a distance d from the surface of the film. Hence, if the film were thick enough, the absolute weight of monomer grafted per unit time should be proportional to film surface area rather than film weight. It follows that the rate of film grafting in grams monomer per unit area per unit time should become constant above a certain film thickness, a type of relationship shown in Figure 9.

As far as the writer can find, the relationship shown in Figure 9 has neither been postulated nor tested in the existing literature on film grafting. One of the objectives of the present research is to carry out an experimental test of the relationship.

B. Mathematical Approach.

The curves for concentration function versus film thickness shown in Figure 8 are hypothetical. Even an approximate theory for computing such curves would be helpful in correlating

and explaining a considerable body of film grafting data. One approach is to set up a differential equation by equating the derivative of concentration with time to the sum of two terms, one term based on Fick's law of diffusion and the other term based on the reaction kinetics of monomer consumption within the film. The solution of such a differential equation results in a concentration function curve of the sort shown in Figure 8. The solution can often be expressed in the form of a mathematical series, where it may be necessary to evaluate several terms in order to compute the concentration curve with acceptable accuracy.

Several concentration curves have been calculated in this way with the aid of our General Electric time sharing computer terminal. Without the computer, the computations would be much too slow to be practical. In this work the computer is more than an aid to computation. It is a research tool which enables the plotting of curves based on various mathematical models (equations) in a short period of time, thus quickly indicating the adequacy or inadequacy of the underlying mathematics. The mathematical research is proceeding simultaneously with the experimental research, but is still only in the preliminary stages.

V. Further Work Planned.

Activation Energy of Grafting: As noted above, a comparison of activation energies of grafting on various polymers is more significant than a simple comparison of rates at room temperature. Temperature control equipment will be required in the measurement of activation energies, and such equipment is presently being ordered. This phase of the research should be completed in the next few months.

Monomer Vapor Grafting: Techniques for grafting of vapor phase monomers on polymer films will be developed using the special apparatus shown in Figure 3. This phase of the work should be fairly well advanced within the next few months.

Equilibrium Concentration of Monomer: Equilibrium concentration of various monomers in various films will be measured by simply weighing the swollen film after immersion in monomer for a period of time. Equilibrium concentration is one of the factors influencing the rate of grafting. The length of time it takes the film to become saturated is related to the rate of monomer diffusion into the film. At some point in this research it may become desirable and necessary to measure diffusion constants for various monomer/polymer pairs.

Effect of Monomer Concentration: One way of studying the effect of monomer concentration is to carry out a series of grafting reactions on film immersed in solutions of monomer at several different concentrations. This phase should be complete within the next few months.

Number of Radical Sites Formed: Irradiation of polymer produces polymeric radicals, and the initiation of monomer polymerization takes place at such free radical sites. The concentration of free radicals in the polymer can be estimated by reaction with a free radical scavenger such as diphenylpicrylhydrazyl (DPPH), followed by determination of combined DPPH using spectrophotometric analysis. Studies of this type will probably be undertaken in the near future.

Polymer-Polymer Grafting: Gamma irradiation of polymethylpentene intimately mixed with some other polymer should produce crosslinking between the two polymers. Almost no data are available in the literature on such polymer-polymer grafting reactions. An attempt will be made to carry out such reactions as part of this research.

Study of Grafting Accelerators: Accounts of the acceleration of grafting by the use of additives such as redox pairs have been published. It is planned to evaluate a few accelerators as part of the present research.

Free Radical Characterization by ESR Spectroscopy: Grafting is initiated by free radicals produced within the polymer film. At some time in the future it is hoped that an ESR spectrometer can be obtained for use in studying the nature of such polymeric radicals.

The use of ESR spectroscopy to characterize polymeric free radicals was well demonstrated by Ohnishi (8). Ohnishi studied the oxidation of polymer films induced by gamma rays from a cobalt source, a set of conditions that parallels the present research in some ways. His results were extensive and detailed. Free radicals produced by irradiation were identified for several polymers, and factors affecting ESR spectra were studied. The concentration of free radicals as well as free radical formation curves were determined for some polymers. The reactions of different types of polymeric radicals with oxygen were followed by the ESR technique.

In the present work, the ESR technique should be valuable in identifying the radicals involved in the grafting mechanism, and in following significant changes in free radical concentration when different techniques of grafting are used.

VI. Acknowledgement.

The writer would like to acknowledge the help of Mr. Donnie Shaw, who assisted in the experimental work and in drawing the figures.

References

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Figure Captions

Figure 1. Unit structures of polyethylene, polypropylene, and polymethylpentene.

Figure 2. High vacuum system for outgassing and removal of oxygen from monomers.

Figure 3. Special apparatus for following the grafting of vapor phase monomer to polymer film.

Figure 4. Grafting of liquid styrene monomer on 0.0107 inch film of polymethylpentene -○ ; 0.009 inch film of polyethylene -□ .

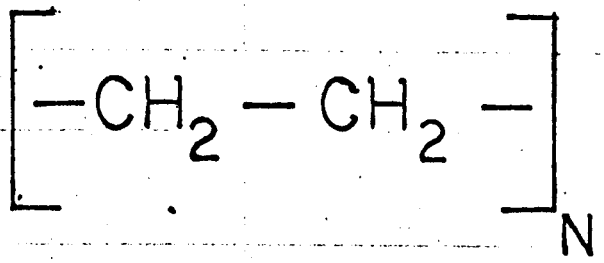
Figure 5. Grafting of liquid styrene -○ and methyl methacrylate - △ on 0.0055 inch film of polymethylpentene.

Figure 6. Grafting versus swelling in styrene for 0.0055 inch polymethylpentene -○ , and 0.009 inch polyethylene - □ .

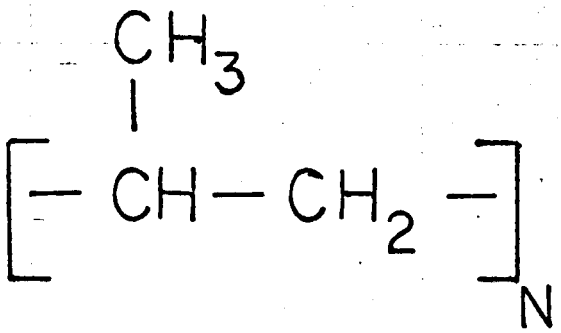
Figure 7. Comparison of styrene grafting on polymethylpentene film of 0.0055 inch thickness -○ and 0.0107 inch thickness - □ .

Figure 8. Hypothetical monomer concentration function versus film thickness compared for a thin film (A) and a thick film (B).

Figure 9. Hypothetical relationship between grams of monomer grafted per unit time per unit surface area and film thickness.



POLYETHYLENE



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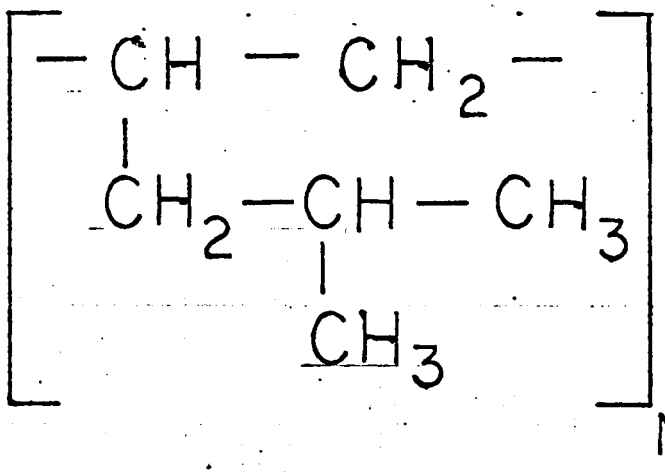

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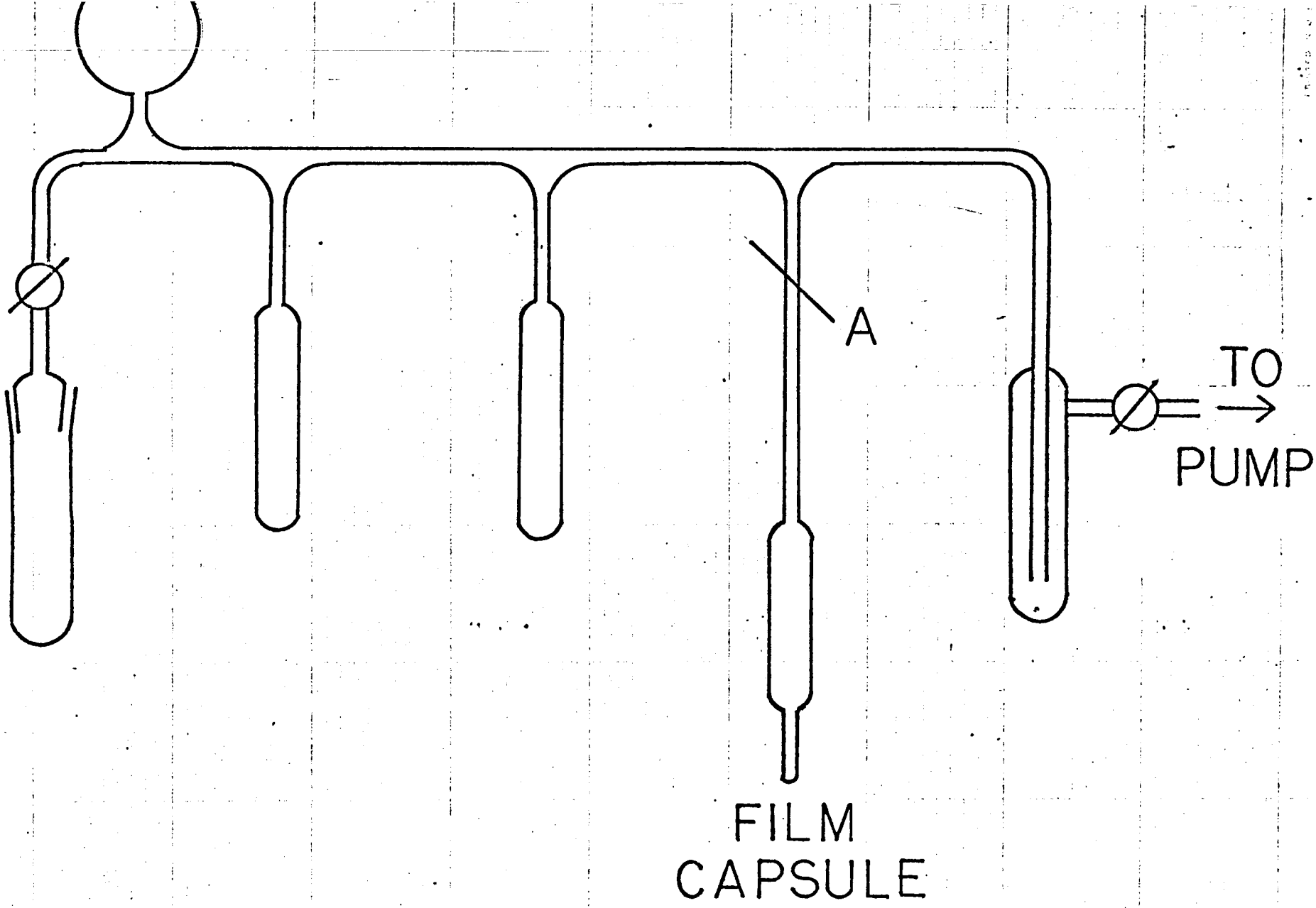
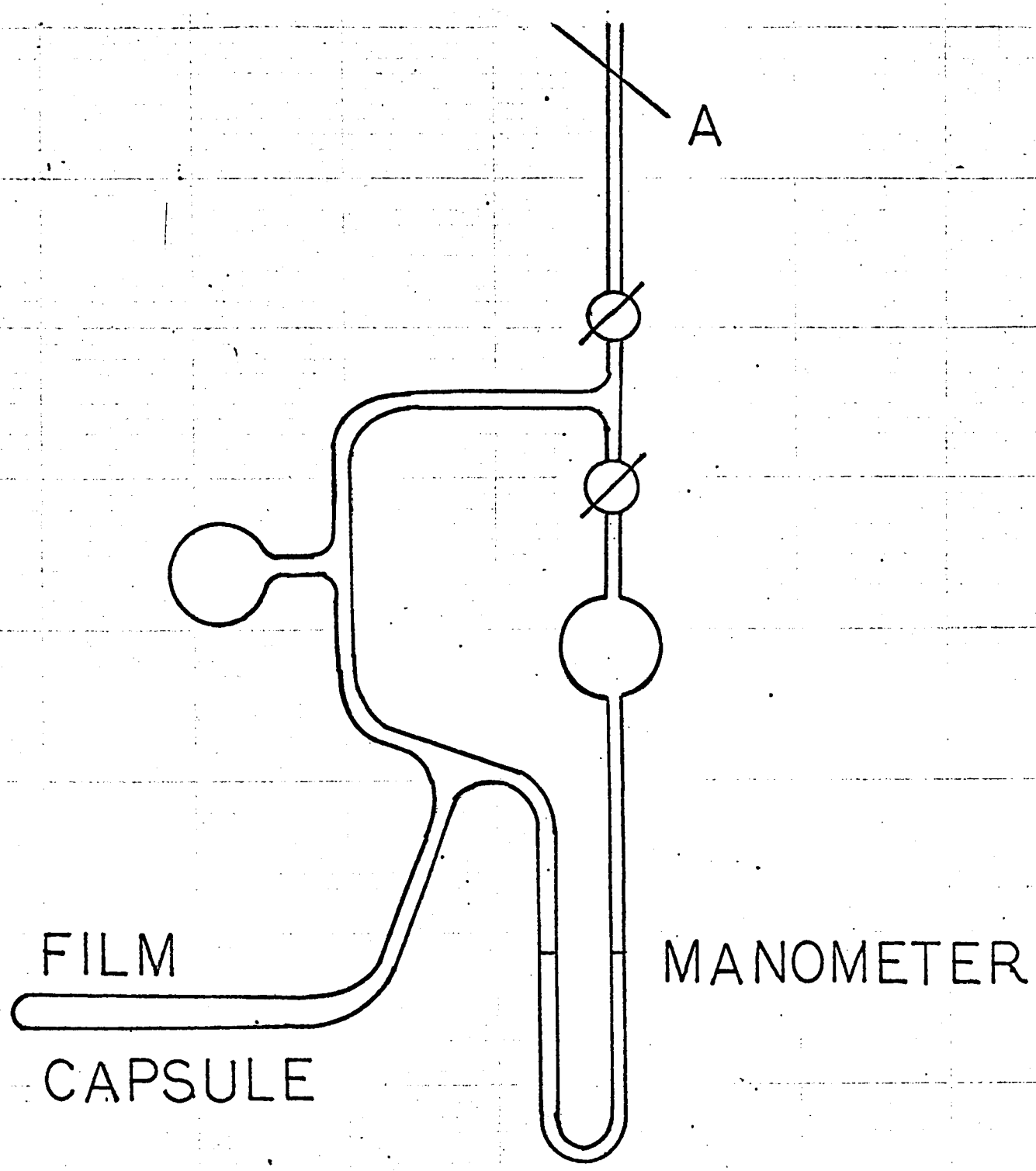


FIG 2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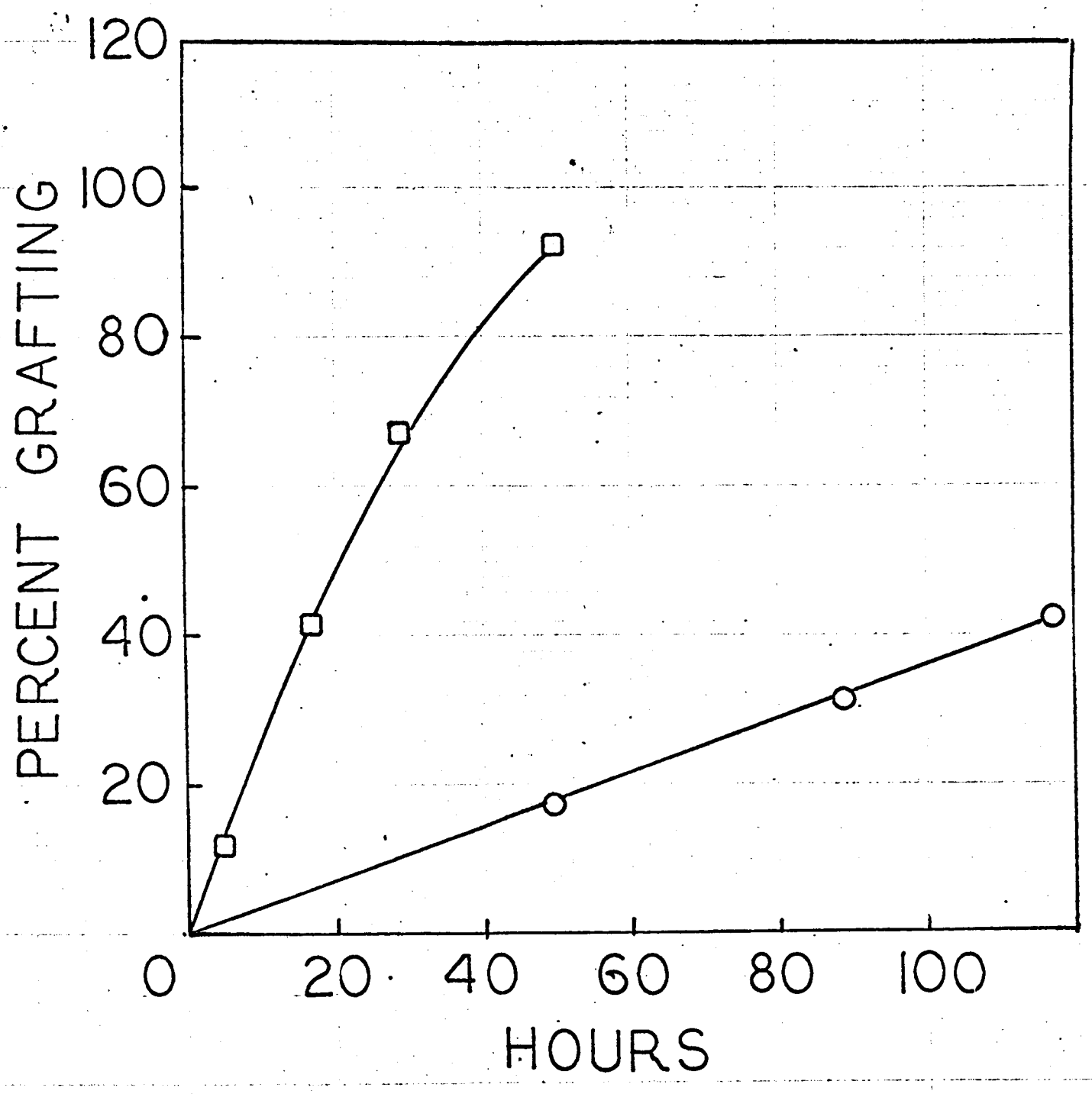
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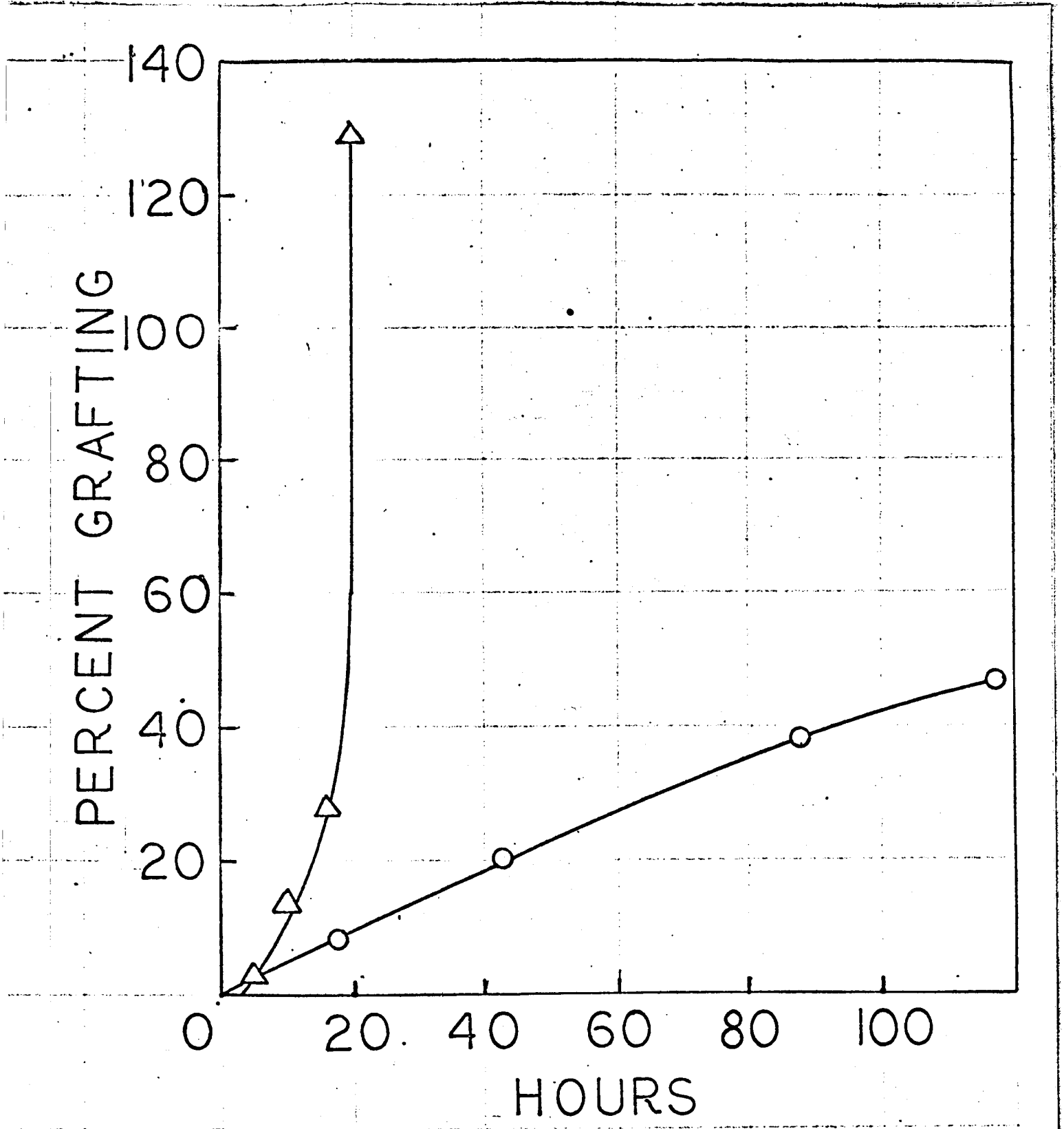
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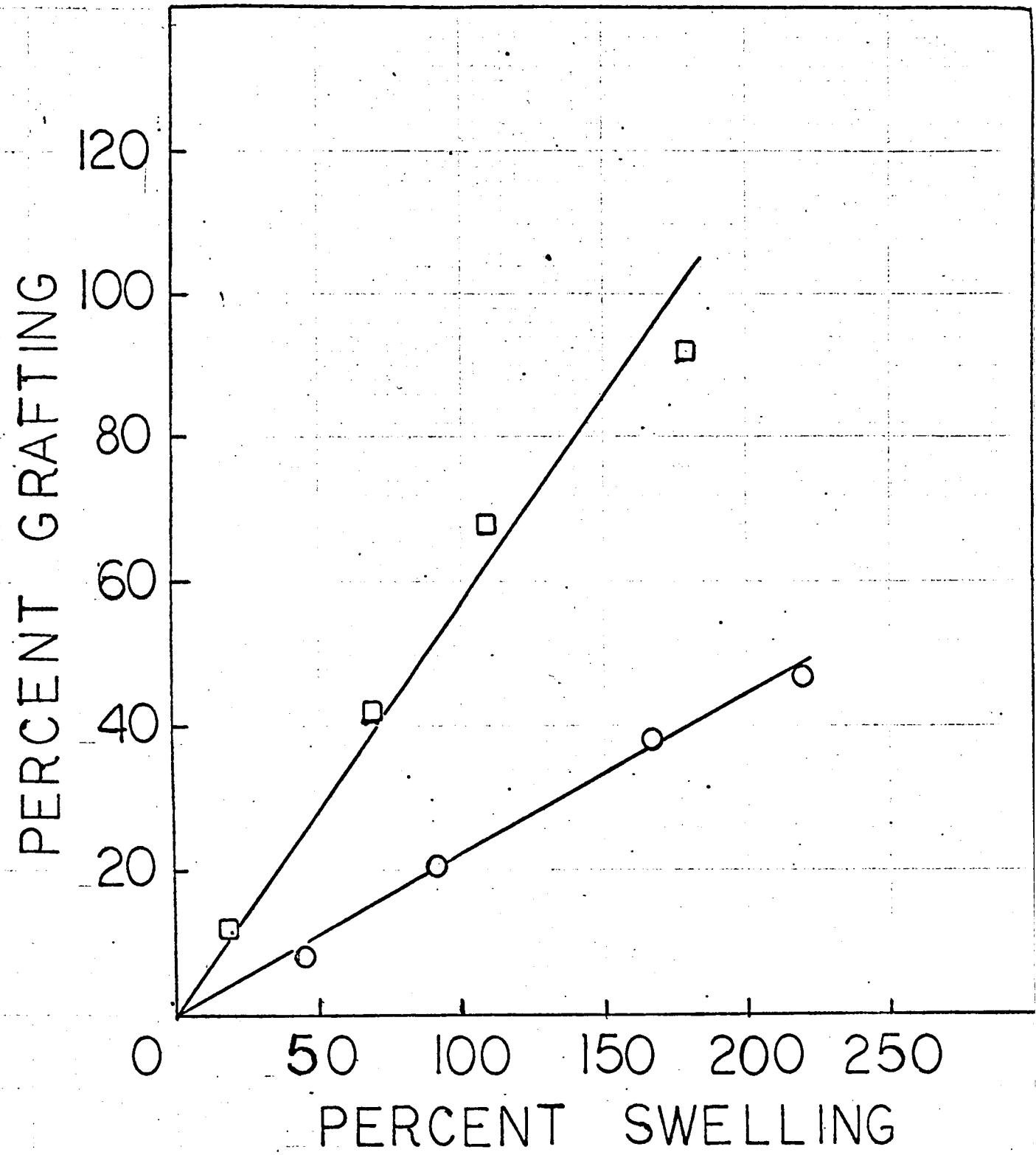
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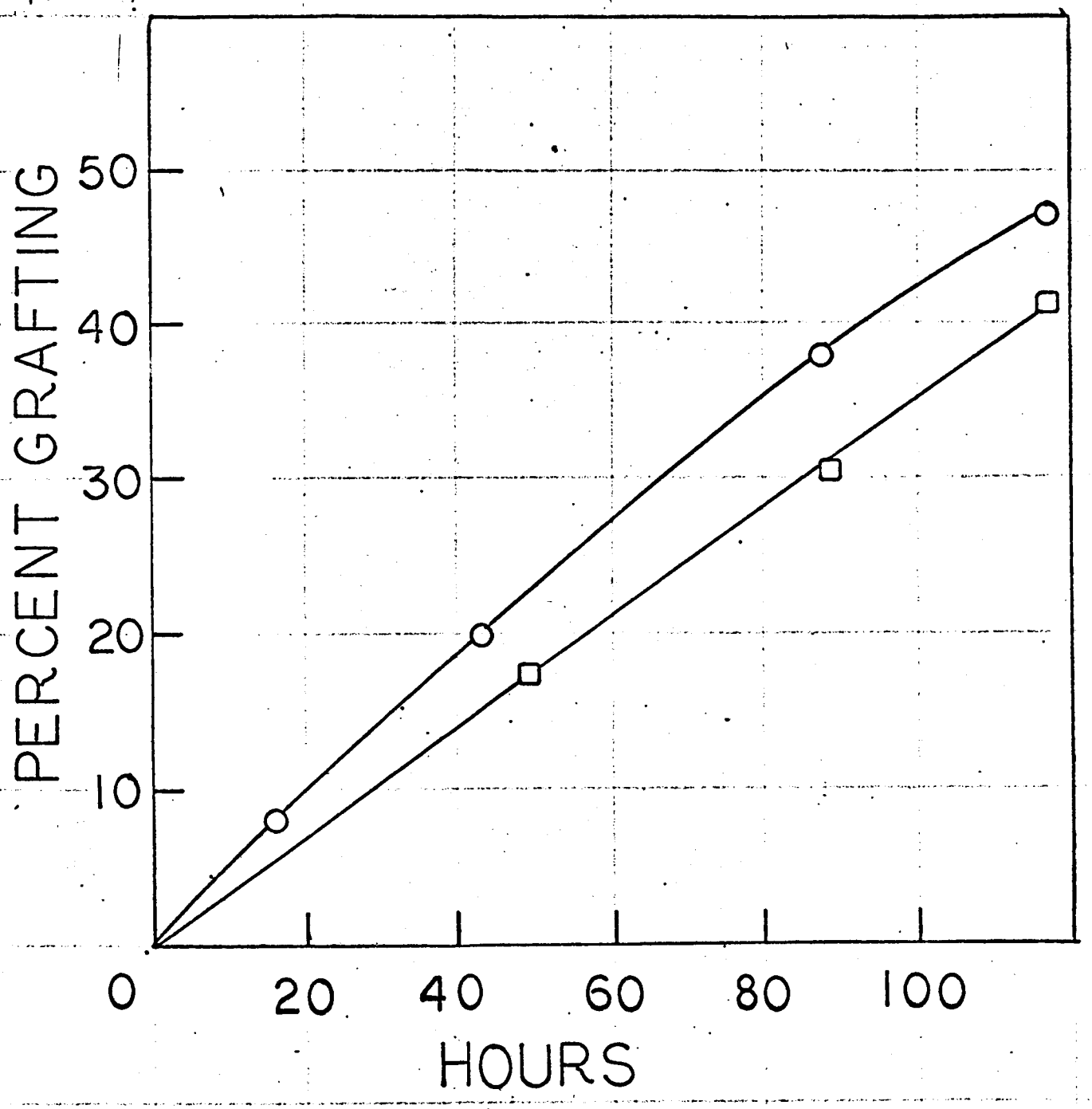
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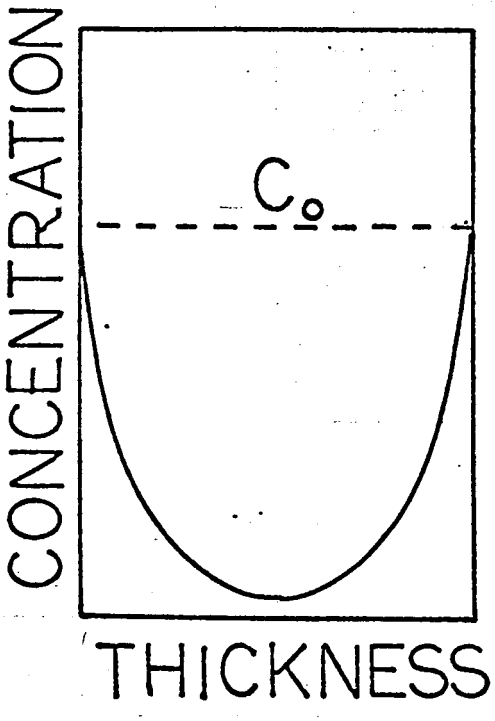

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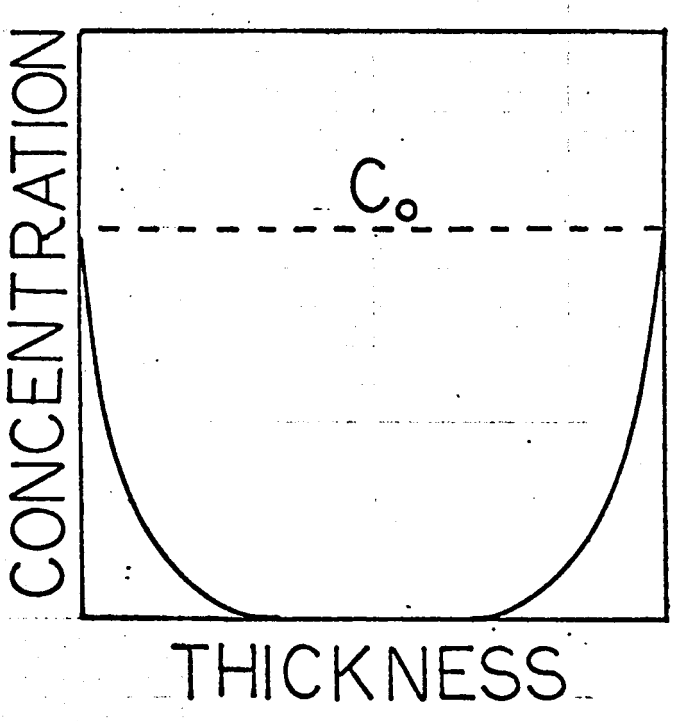

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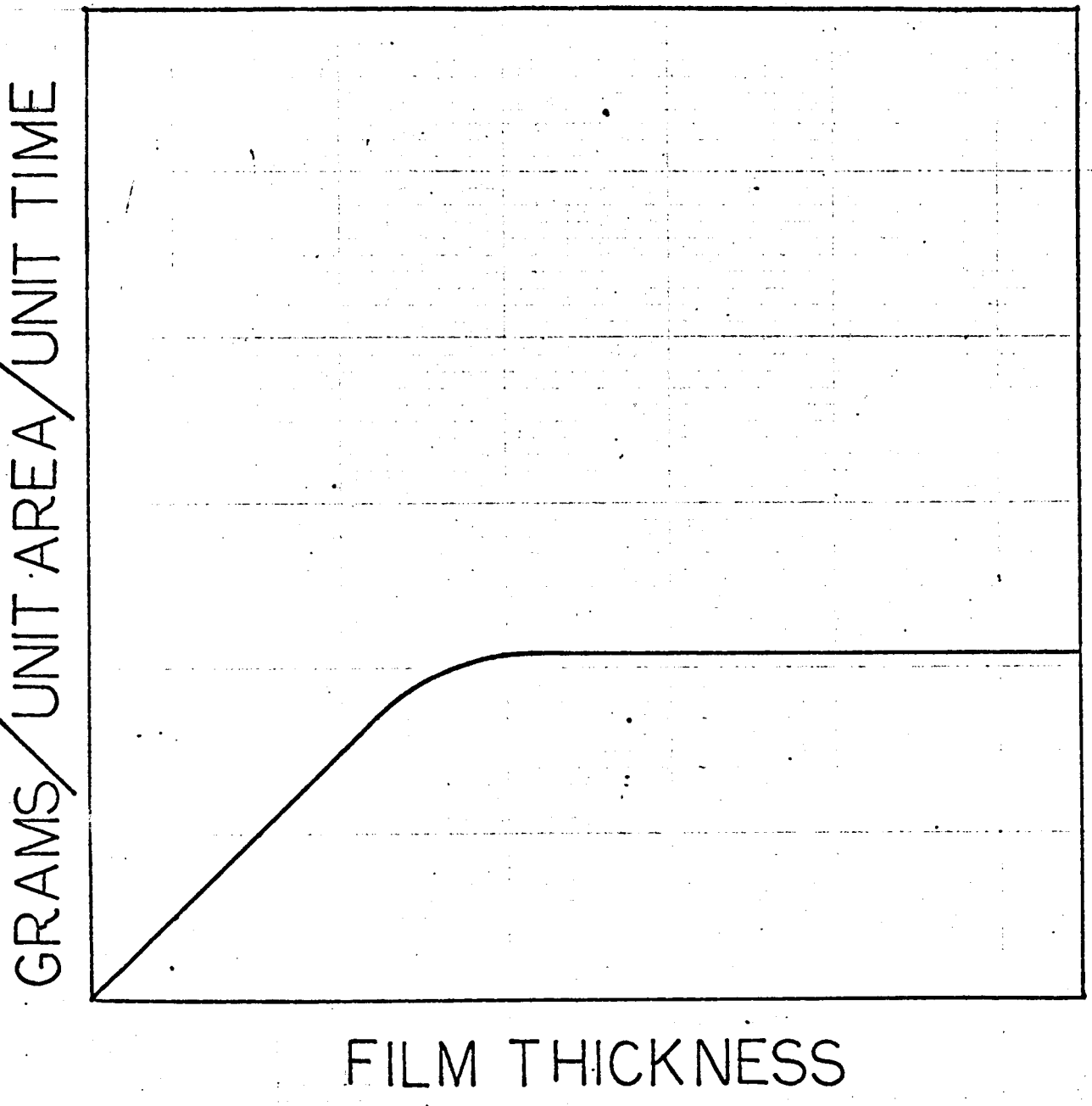
GRAMS/UNIT AREA/UNIT TIME
FILM THICKNESS